Conducting absorbent composite for parallel plate chemicapacitive microsensors with improved selectivity

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ABSTRACT

Conducting absorbent composites were prepared using two organic polymers (polar and nonpolar) mixed with conductive carbon nanoparticles and an ionic liquid ($BMIPF_6$). The mixture was deposited between the plates of chemicapacitive microsensors using ink-jet technology. Different coatings were characterized using SEM and DRIFTS techniques. The response magnitude for each sensor depends on numerous phenomenon but changes in permittivity of the analyte and polymer swelling dominate. The performance of individual chemicapacitive sensors were characterized through exposure to concentrations of various volatile organic compounds with different functional groups in a climate controlled vapor delivery system. Sensitivity, selectivity and limits of detection, of each prepared sensor, were compared and the discrimination power was evaluated using quadratic discriminant analysis. Ionic liquid doped polymers were able to enhance the sensitivity and the selectivity of parallel plate capacitive sensors. Improved analyte classification was achieved with the ionic liquid-doped polymers (97% accuracy) over the pure polymers. This preliminary study describes the first use of polymer composites with carbon black and ionic liquids as the absorbent dielectric layer in parallel plate microcapacitive sensors.

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1. Introduction

Among chemical sensing techniques, thin absorbent polymer films with a sensitive transducer are well suited for low power, low-cost and portable applications [1–3]. Polymers are selected based on their ability to form stronger reversible hydrogen bonds, van der Waals bonds, and dipole–dipole interactions with some analytes over others [1]. Using multiple sensors in the array can mitigate cross-sensitivities resulting in improved selectivity and reduce requirements of chromatography. Parallel plate chemicapacitive microsensors with absorbent polymer coatings have been successfully used to detect a wide range of volatile organic chemicals [1,4]. These microsensors have been employed as the detector in commercially available mini gas chromatographs because of their small size and ability to operate in air [5]. Typically individual parallel plate capacitors are filled or partially filled with selectively absorbing polymers. When exposed to volatile analytes, absorption of the chemical into the polymer film alters the permittivity of the polymers resulting in changes in the capacitance of the sensor elements.

Dozens of polymers have been studied for use with these systems in order to maximize sensor response at a given analyte concentration (maximize sensor sensitivity) and improve selectivity [1–3,6,7]. We hypothesized that the magnitude of this change in capacitance results from a complex combination of response phenomena that depends on five factors: (1) dielectric chemical structure modification from reversible weak interactions with the analyte; (2) dielectric swelling due to absorption of the analyte which reduce dipole moments within the polymer altering its permittivity and conductivity; (3) the affect of the analyte on the ability of the polymer (or its side groups) to be polarized in the electric field (i.e. crosslinking or loosening of side groups that may be physically hindered); (4) the permittivity of the analyte being absorbed; and (5) the amount of analyte that absorbs into the dielectric.

The swelling effect in sensors has been utilized to enhance the sensitivity of chemresistors [8,9]. This is typically done by combining a conductor (carbon black (CB) particles) with a selectively absorbent polymer [8,10]. The applicability of conducting materials to enhance the sensitivity and modify the selectivity of a polymer matrix in parallel plate chemicapacitor sensors has not been previously investigated and is the focus of this work (Fig. 1). A charge to
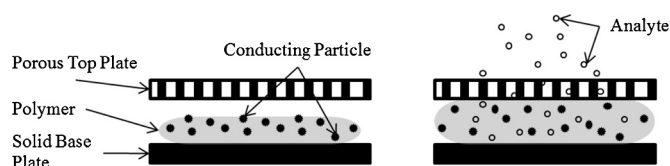
Fig. 1. Conducting particles are mixed with functionalized polymers and deposited between the microcapacitor plates. The polymer swells as it absorbs the analyte resulting in a significant change in capacitance and a larger sensor response when compared to pure polymer.

Table 1
Prepared polymer nanocomposites and ionic liquid polymer composites mixtures.

Non-polar polymer	Polar polymer	Ionic liquid/polymer
PDMS	OV275	$BMIPF_6$
PDMS/20% CB	OV275/30% CB	OV275/10% $BMIPF_6$
		PDMS/10% $BMIPF_6$

voltage converting circuit was used to extract the capacitance signal of the chemicapacitor sensors through the use of an embedded microcontroller [1].

Nonlinear contributions from swelling effects following analyte absorption can make the interpretation of capacitance change complex [3,10]. Analyte adsorption phenomena on a polymer surface can also play a major role in sensor response and is related to polymer film thickness [3]. Sensor responses are related to dielectric chemical structure modifications due to different chemical and physical interactions, swelling effects, and the amount and the permittivity of the analyte absorbed or adsorbed to the polymer [11–14]. When the polymer matrix swells during exposure, the effective polymer volume (density of dipole moments) between the capacitor plates decrease, lowering the sensor response [1]. We observe an increase in chemicapacitor response amplitude from incorporating conducting particles in to the polymer [8]. The polymer matrix will swell during exposure to analyte, increasing the average distance between conducting particles. This can increase the charge holding capacity of the sensor leading to enhanced capacitance changes and a more sensitive (larger sensor response to the same analyte concentration) system.

Carbon black nanoparticles and ionic liquids were mixed with polymers to enhance the sensitivity and selectivity of microsensors. Carbon black particles aggregated during the coating process causing sensor preparation difficulties. The ionic liquid ($BMIPF_6$) had no obvious aggregation resulting in a better distribution in the matrix. $BMIPF_6$ was chosen for study based on several factors including its density, viscosity, volatility and the level of interactions with VOCs. Gel like ionic liquids such as $BMIPF_6$ are easy to coat on microsensors and this also tends to be the best physical state for greater absorption of volatile organic compounds. $BMIPF_6$ is also economical and readily available and has been used in quartz crystal microbalance applications [15]. Two polymers extensively studied in sensor and chromatography applications, polydimethyl siloxane (PDMS) and polycyanopropyl siloxane (OV275) have been used for form the composites.

Polymer-based sensors can be used to detect most volatile and semi-volatile organic compounds with a boiling point in the range of 40–200 °C. Highly volatile chemicals that boil below 40 °C do not partition well into polymers and those that boil above 200 °C tend to have vapor pressures that are too low for vapor phase detection. Other materials have been used to broaden the range of detectable chemicals including high surface area functionalized sol–gels used in the detection of carbon dioxide [16] although such materials often have to be heated to achieve optimal performance [1].

A number of microfabricated transducers have been developed that utilize polymers to selectively absorb VOCs. Examples include those that measure polymer swelling including resistive sensors [17] and cantilever stress sensors [18], resonating cantilevers, surface acoustic wave (SAW) devices [19], quartz crystal microsensors (QCM) [20], and flexural plate wave (FPW) sensors [21] that measure mass and viscoelasticity changes, and capacitive sensors [11] (used in this study) which measure changes in polymer permittivity.

Chemicapacitors use two basic geometries, interdigitated electrodes and parallel-plate configurations. Interdigitated electrodes employ single layers of metal either slightly elevated [22] or deposited on a substrate to form meshed combs. The absorbent material is then deposited onto the electrodes. Parallel-plate sensors [23] (this study) consist of a layer of metal deposited on a substrate, a layer of polymer and a second, porous layer of metal above the polymer. Details on the specific capacitive transducer used in this study can be found in the section below.

2. Materials and methods

2.1. Sensor design

The sensor chips used in this study were fabricated using the Multi-User MEMS Process [24] (MUMPs; MEMSCAP). The capacitive sensors were designed and donated by Seacoast Science. Each capacitor is a 285 μm square and has a perforated top plate suspended over a solid bottom plate, with a 0.75 μm gap between the plates with a base (unfilled) capacitance of ~1 pF. The gap is filled with a polymer that is injected through a porous top plate. All sensor chips measured 3 mm × 2 mm and had 3 parallel-plate capacitors. The capacitor plates were made of conductive polycrystalline silicon consisting of a 0.5 μm-thick bottom plate resting on the substrate, an air gap that was filled with polymer subsequent to the MEMS fabrication process, and a 2 μm-thick ventilated top plate. The top plate was anchored to the substrate with posts at approximately 60 μm intervals in order to minimize flexing when the polymer absorbed VOCs and swelled. The top plate also had 5 μm × 5 μm square holes separated by about 2.5 μm [25]. These holes were required for removal of a sacrificial silicon oxide layer during fabrication but also allow analyte vapors to pass through to the sorbent polymer.

Polydimethyl siloxane (PDMS), poly (cyanopropyl siloxane) (OV275), 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIPF_6$) (ionic liquid), and carbon black nanoparticles (~50 nm) were purchased from Sigma Aldrich. Polymer/carbon black (CB) nanocomposites were prepared in different proportions to determine optimum CB to PDMS and OV275 ratios. These mixtures proved to be problematic because clumping of the nanoparticles cause difficulties in the ink jet coating process. Thus only one mixture of each was successfully prepared. Ionic liquid/polymer mixtures mixed well and coated sensors without problems. $BMIPF_6$ and polymer structures are illustrated in Fig. 2.

2.2. Polymers and conductors/preparation

Polymer nanocomposite were prepared according to Table 1 weight ratios. These nanocomposites were diluted to approximately 0.1 wt% with the proper solvents (trichloromethane for nonpolar polymers and acetone for polar polymers) before being introduced into the (0.75 μm) gap between the sensor plates using an ink jet. The coating is applied until the sensor baseline readings become static – at this point the coating is believed to be very close to 0.75 μm. The sensors are placed under a nitrogen flow and then heated for 30 min at 80 °C to completely remove any of the solvent. This likely results in a coating that is slightly less than 0.75 μm thick. The swelling that occurs upon exposure to analytes causes the